Electron Correlation and Jahn-Teller Interaction in Manganese Oxides

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Abstract

The interplay between the electron repulsion U and the Jahn-Teller electron-phonon interation $E_{\rm LR}$ is studied with a large d model for the ferromagnetic state of the manganese oxides. These two interactions collaborate to induce the local isospin (orbital) moments and reduce the bandwidth B. Especially the retardation effect of the Jahn-Teller phonon with the frequency Ω is effective to reduce B, but the strong Ω-dependence occurs even when the Coulombic interaction is dominating ($U >> E_{\rm LR}$) as long as $E_{\rm LR} > \Omega$. The phonon spectrum consists of two components, i.e., the temperature independent sharp peak at $\omega = \tilde{\Omega} = \Omega[(U + 4E_{\rm LR})/U]^{1/2}$ and that corresponding to the Kondo peak. These results compared with the experiments suggest that $\Omega < E_{\rm LR} < U$ in the metallic manganese oxides.

74.25.Fy, 74.25.Ha, 74.72.-h, 75.20.Hr

Since the discovery of colossal magnetoresistance (CMR) the manganese oxides $Re_{1-x}A_xMnO_3$ (Re: rare earth metal ion, A: divalent metal ion) have been attracting intensive interest recently [1]. One of the controversial issues is the role of orbital degeneracy of e_g-electrons. In the conventional models of these compounds [2–5], the strong Hund's coupling is considered to be of primary importance and the orbital degeneracy has been often neglected. Recently, however, Millis *et al.* [6,7] correctly pointed out that the Hund's coupling alone is not enough to explain the CMR together with the insulating temperature dependence of the resistivity $\rho(T)$ above the ferromagnetic transition temperature T_c. The additional coupling they proposed to be important is the Jahn-Teller electron-phonon coupling, which lifts the double degeneracy of e_g orbitals and gives rise to the polaronic effect. The small polaron formation above T_c leads to the insulating $\rho(T)$. In contrast with the insulating phase, the spin alignment below T_c will enlarge the band width B as $B \propto \cos(\theta_{ij}/2)$ (θ_{ij} is the angle between the two neighboring spins $\vec{S}_i$ and $\vec{S}_j$), and the Jahn-Teller interaction enters the weak coupling regime. This scenario seems to be consistent with the large isotope effect on T_c by replacing O^{16} by O^{18} [8].

The strong correlation models of these compounds have been also studied by several authors especially for the undoped cases [9,10]. In these models the Jahn-Teller interaction is considered to be smaller than the Coulomb interactions, and the effective Hamiltonian for the spin-orbital coupled system and its phase diagram have been clarified. It is rather natural to assume the strong electron correlation because the strong Hund's coupling originates from the strong electron-electron interactions ($\sim$ 5eV). However, it is not trivial if the electron-electron interaction continues to be strong even in the effective Hamiltonian describing the low energy physics after the screening by oxygen orbitals and conduction electrons, and it still remains the controversial issue whether the electron-electron interation and/or the Jahn-Teller coupling are in the strong coupling regime or not.

Experimentally there are several anomalous features which cannot be explained by the weak Jahn-Teller coupling described above even in the low temperature ferromagnetic phase below T_c.

[a] In the neutron scattering experiment no temperature dependent phonon modes have been observed [11]. The recent Raman scattering experiment also shows that the Jahn-Teller phonons (especially their frequencies) are temperature independent and insensitive to the ferromagnetic transition at T_c [12].

[b] The photo-emission spectra show a small discontinuity at the Fermi edge even at $T << T_c$, which suggests some interactions still remain strong there [13].

[c] The optical conductivity $\sigma(\omega)$ at $T << T_c$ is composed of two components, i.e., the narrow Drude peak ($\omega < 0.02$eV) and the broad incoherent component extending up to $\omega \sim 1$eV [14]. The Drude weight is very small, which seems to be consistent with the photo-emission spectra.

[d] The low temperature resistivity $\rho(T)$ can be fitted by

$$\rho(T) = \rho_0 + AT^2, \tag{1}$$

where A is a large constant of the order of $500\mu\Omega\text{cm/K}^2$ [15], again suggesting the strong electron correlation.

[e] Contrary to the case of resistivity [d], the coefficient of T-linear specific heat is very small with $\gamma = 2\text{mJ/K}$, which violates the Kadowaki-Woods law for these compounds [16].

Although [e] is difficult to reconcile with [a]-[d], we consider the latter as the evidences for the strong coupling even at $T \ll T_c$. Because the spins are perfectly aligned at $T \ll T_c$, the only remaining degrees of freedom are the orbital ones. In this paper, we study a large d model [17] for the ferromagnetic state including both the electron-electron interaction U and the Jahn-Teller coupling g. This is the generalization of Ref.[7] in two respects, (i) including the electron-electron interation, (ii) including the quantum fluctuations. Especially the latter is essential to describe the low temperature Fermi liquid state, which is described by the Kondo peak in the large d limit [17]. The strong electron-electron interaction with the reasonable magnitude of the Jahn-Teller coupling explains both the large isotope effect and [a]. Moreover, the features of strong correlation [b]-[d] are at least consistent with the large U picture although [e] still requires further studies, which we have not undertaken in this

paper.

We start with the Hubbard-Holstein model for the ferromagnetic state.

$$H = -\sum_{i,j,\alpha,\alpha'} t_{ij}^{\alpha\alpha'} c_{i\alpha}^{\dagger} c_{j\alpha'} + U\sum_{i} n_{i\uparrow} n_{i\downarrow} \\ - g\sum_{i} Q_i (n_{i\uparrow} - n_{i\downarrow}) + \frac{1}{2}\sum_{i} (\frac{P_i^2}{M} + M\Omega^2 Q_i^2), \tag{2}$$

where the spin indices $\alpha = \uparrow, \downarrow$ correspond to the orbital degrees of freedom as $\uparrow = d_{x^2-y^2}$ and $\downarrow = d_{3z^2-r^2}$, and the real spins are assumed to be perfectly aligned. We consider only one Jahn-Teller displacement mode Q_i for each site, while there are two modes Q_{2i}, Q_{3i} in the real perovskite structure [18]. However this does not change the qualitative features obtained below. The Jahn-Teller mode is assumed to be an Einstein phonon with a frequency Ω. The transfer integral $t_{ij}^{\alpha\alpha'}$ depends on a pair of orbitals (α, α') and the hopping direction. These dependences lead to the various low lying orbital configurations, and thus they suppress the orbital orderings in the ferromagnetic state. Actually there are no experimental evidences for the orbital orderings, e.g., the anisotropies of the lattice constants and/or transport properties in the ferromagnetic state. Then we assume that no orbital ordering occurs down to the zero temperature due to the quantum fluctuations, and the transfer integral is assumed to be diagonal for simplicity, i.e., $t_{ij}^{\alpha\alpha'} = t_{ij}\delta_{\alpha\alpha'}$. This means that the ground state is a Fermi liquid with two degenerate bands at the Fermi energy. In order to describe this Fermi liquid state, we employ the large-d approach where the model Eq.(2) is mapped to the impurity Anderson model with the self-consistent condition [17]. This approach has been applied to the manganese oxides to study the Hund's coupling by Furukawa [5] and to study the additional Jahn-Teller coupling by Millis *et al.* [7]. The action for the effective impurity model is given by

$$S = \int_0^\beta d\tau \int_0^\beta d\tau' c_\alpha^{\dagger}(\tau) G_0^{-1}(\tau - \tau') c_\alpha(\tau') \\ + \int_0^\beta d\tau \Big[U n_\uparrow(\tau) n_\downarrow(\tau) - g Q(\tau)(n_\uparrow(\tau) - n_\downarrow(\tau)) \Big] + \int_0^\beta d\tau \frac{M}{2} \Big[(\partial_\tau Q(\tau))^2 + \Omega^2 Q(\tau)^2 \Big], \tag{3}$$

where $G_0^{-1}(\tau - \tau')$ is the dynamical Weiss field representing the influence from the surrounding sites. The self-consistency condition is that the on-site Green's function $G(i\omega_n) =$

$(G_0(i\omega_n)^{-1} - \Sigma(i\omega_n))^{-1}$ should be equal to the Hilbert transform of the density of states $D(\varepsilon)$ as

$$G(i\omega_n) = \int d\varepsilon \, \frac{D(\varepsilon)}{i\omega_n + \mu - \Sigma(i\omega_n) - \varepsilon}. \tag{4}$$

We take the Lorentzian density of states $D(\varepsilon) = t/(\pi(\varepsilon^2 + t^2))$ because there is no need to solve the self-consistency equation in this case, and the Weiss field is given by

$$G_0^{-1}(i\omega_n) = i\omega_n + \mu + i\, t \,\mathrm{sign}\,\omega_n. \tag{5}$$

The only unknown quantity is the chemical potential μ, which is determined by the electron number. The determination of chemical potential requires some numerical calculations, but our discussion below is not sensitive to the location of the chemical potential. Then we take μ as the parameter of our model, and the problem is now completely reduced to that of a single impurity. Now we introduce a Stratonovich-Hubbard (SH) field $\xi(\tau)$ to represent the Coulomb interaction U. Then the action is given by

$$\begin{aligned} S = &\sum_{\omega_n} (i\omega_n + \mu + i\, t \,\mathrm{sign}\,\omega_n) c_\alpha^\dagger(\omega_n) c_\alpha(\omega_n) \\ &+ \int_0^\beta d\tau \Big[\frac{\Delta^2}{U} \xi(\tau)^2 + \frac{M}{2} [(\partial_\tau Q(\tau))^2 + \Omega^2 Q(\tau)^2] + \zeta(\tau) Q(\tau) - (\Delta\xi(\tau) + g Q(\tau))(n_\uparrow(\tau) - n_\downarrow(\tau)) \Big], \end{aligned} \tag{6}$$

where $\Delta = (t^2 + \mu^2)/t$ and $\zeta(\tau)$ is the test field to measure the phonon correlation function. At this stage the electron is coupled with the linear combination of the SH field ξ and the phonon Q as $\eta(\tau) \equiv \xi(\tau) + \frac{g}{\Delta} Q(\tau)$. Then the effective action can be derived as

$$\begin{aligned} S = &\sum_{\omega_n} \Big[(i\omega_n + \mu + it\mathrm{sign}\omega_n) c_\alpha^\dagger(\omega_n) c_\alpha(\omega_n) - \Delta\eta(i\omega_n)(n_\uparrow(-i\omega_n) - n_\downarrow(-i\omega_n)) \Big] \\ &+ \sum_{\omega_n} \frac{1}{2M(\omega_n^2 + \tilde{\Omega}^2)} \Big[-\zeta(i\omega_n)\zeta(-i\omega_n) + \frac{2\Delta^2}{U} M(\omega_n^2 + \Omega^2) \eta(i\omega_n)\eta(-i\omega_n) \\ &+ \frac{2g\Delta}{U} (\zeta(i\omega_n)\eta(-i\omega_n) + \eta(i\omega_n)\zeta(-i\omega_n)) \Big], \end{aligned} \tag{7}$$

where $\tilde{\Omega} = \Omega\sqrt{U_{\text{eff.}}/U}$. The effective interaction $U_{\text{eff.}}$ is the sum of the Coulomb repulsion U and the lattice relaxation energy $E_{\text{LR}} = g^2/(2M\Omega^2)$ as $U_{\text{eff.}} = U + 4E_{\text{LR}}$. The phonon Green's function $d(i\omega_n) = \langle Q(\ i\omega_n) Q(-i\omega_n) \rangle$ is given by

$$d(i\omega_n) = \frac{1}{M(\omega_n^2 + \tilde{\Omega}^2)} + 4\Big(\frac{g\Delta/U}{M(\omega_n^2 + \tilde{\Omega}^2)}\Big)^2 \chi_\eta(i\omega_n), \tag{8}$$

where $\chi_\eta(i\omega_n) = \langle \eta(i\omega_n)\eta(-i\omega_n)\rangle$ is the orbital susceptibility of the electronic system. The first term is the usual phonon Green's function with the renormalized frequency $\tilde{\Omega}$, which is higher than the bare Ω. This $\tilde{\Omega}$ does not depend on the electron response function and hence temperature independent. When $U \ll E_{\rm LR}$, $\tilde{\Omega}$ is much larger than Ω and the first term of Eq.(8) is irrelevant in the phonon frequency region $\omega \sim \Omega \sim 0.1$eV. In the opposite limit $U \gg E_{\rm LR}$, the renormalization of the phonon frequency is small. The second term depends on the temperature (Kohn anomaly) and shows the characteristic lineshape with the broadening. From the above consideration together with the experimental fact that no temperture dependence of the phonon frequency has been observed, we conclude that the Coulomb interaction U is larger than the lattice relaxation energy $E_{\rm LR}$.

Now let us study the electronic system in detail. Following Hamann [19], we can obtain the solution of the integral equation for the electron Green's function in the presence of the time-dependent field $\eta(\tau)$, and hence for the effective action. The result is

$$\begin{aligned} S_{\rm eff.} = & \sum_{\omega_n} \frac{\Delta^2}{U} \frac{\omega_n^2 + \Omega^2}{\omega_n^2 + \tilde{\Omega}^2} \eta(i\omega_n)\eta(-i\omega_n) \\ & - \int_0^\beta d\tau \frac{2\Delta}{\pi}\Big[\eta(\tau)\tan^{-1}\eta(\tau) - \frac{1}{2}\ln(1+\eta(\tau)^2)\Big] \\ & + \frac{1}{\pi^2}\int_0^\beta d\tau \int_0^\beta d\tau' P\frac{1}{\tau-\tau'}\eta(\tau)\frac{d\eta(\tau')}{d\tau'}\frac{1}{\eta(\tau)^2-\eta(\tau')^2}\ln\frac{1+\eta(\tau)^2}{1+\eta(\tau')^2}, \end{aligned} \tag{9}$$

where P denotes the principal value. The Eq.(9) differs from Eqs.(3.40)-(3.43) of Ref. [19] by the frequency dependent coefficient of $\eta(i\omega_n)\eta(-i\omega_n)$ due to the retardation effect of the phonons. A similar model without the Coulomb repulsion U has been studied by Yu-Anderson [20], which corresponds to the limit $U \to 0, \tilde{\Omega} \to \infty, \tilde{\Omega}^2 U =$ finite in Eq.(9). First, we consider the saddle point solution for the η field assuming the static configuration $\eta(\tau) = \eta_0$. Then the action for the static solution becomes

$$S_0 = \beta\Big[\frac{\Delta^2}{U_{\rm eff.}}\eta_0^2 - \frac{2\Delta}{\pi}\Big(\eta_0\tan^{-1}\eta_0 - \frac{1}{2}\ln(1+\eta_0^2)\Big)\Big]. \tag{10}$$

When $U_{\rm eff.}/(\pi\Delta) < 1$, there is a single minimum at the origin, and the double minima appear

for $U_{\rm eff.}/(\pi\Delta) > 1$. We are interested in the limit of strong correlation $U_{\rm eff.}/(\pi\Delta) >> 1$, and in this limit the tunneling events (instantons) between the two minima at $\eta = \pm\eta_0 \cong \pm\frac{U_{\rm eff.}}{2\Delta}$ play an essential role in producing the Kondo peak at the Fermi level. The third term in Eq.(9) gives the non-local interaction between the instantons along the time axis, which corresponds to J_z term when it is mapped to the Kondo problem. The fugacity z of the instanton, which corresponds to $J_\perp$, can be estimated following ref. [19]. Let τ_0 be the width of the instanton, i.e., hopping time, and the action for a single instanton is given by

$$S_{\rm inst.}(\tau_0) = \sum_{\omega_n} \frac{2g^2\Delta^2\omega_n^2}{U^2 M(\omega_n^2+\tilde{\Omega}^2)\tilde{\Omega}^2}\ \eta_{\rm inst.}(i\omega_n)\eta_{\rm inst.}(-i\omega_n) + \frac{1}{6}\tau_0 U_{\rm eff.} - \ln\tau_0. \tag{11}$$

The last term can be written in terms of the derivative $h(\tau) = d\eta_{\rm inst.}(\tau)/d\tau$, which is the localized function around the center of the instanton ($\tau = 0$) with the width of the order of τ_0 and the integral of $h(\tau)$ over τ is $2\,\eta_0$. We assume $h(\tau) = (\eta_0/\tau_0)e^{-|\tau|/\tau_0}$. Then the summation over ω_n can be easily done and we obtain

$$S_{\rm inst.}(\tau_0) = \frac{4E_{\rm LR}}{\Omega^2\tau_0} f(\tilde{\Omega}\tau_0) + \frac{1}{6}\tau_0 U_{\rm eff.} - \ln\tau_0, \tag{12}$$

where $f(\alpha) = \alpha(\alpha+2)/(4(1+\alpha)^2)$. Minimizing $S_{\rm inst.}(\tau_0)$ with respect to τ_0, we obtain τ_0 as $\tau_0 \cong 6/U_{\rm eff.}$ for $U_{\rm eff.} >> 6\tilde{\Omega}$ and $\tau_0 \cong 3/U_{\rm eff.} + \sqrt{(3/U_{\rm eff.})^2 + 6E_{\rm LR}/(\Omega^2 U_{\rm eff.})}$ for $U_{\rm eff.} << 6\tilde{\Omega}$. Introducing the dimensionless variables $x = E_{\rm LR}/\Omega$ and $y = U/E_{\rm LR}$, the reduction factor R for the instanton fugacity $z = \eta_0^{-1}e^{-R}$ is given by

$$R = 2x\sqrt{1+4y^{-1}}, \quad \text{for } \ y >> 1/\max(x, x^2) \tag{13}$$

$$R = \sqrt{1+\frac{2}{3}x^2(4+y)}, \quad \text{for } \ y << 1/\max(x, x^2). \tag{14}$$

The main conclusion here is that when $x > 1$, i.e., $E_{\rm LR} > \Omega$, the reduction factor R is proportional to x even in the limit $U \gg E_{\rm LR}$. This is because the overlap of the phonon wavefunction enters the tunneling matrix element even when the Coulomb interaction is dominating.

In summary, the fugacity of the instantons and the long range interaction between them can be mapped to the anisotropic Kondo model with the Kondo couplings given by

$$N(0)J_\perp \cong \frac{\Delta}{U_{\rm eff.}} e^{-R}$$
$$N(0)J_z \cong \frac{\Delta}{U_{\rm eff.}}, \tag{15}$$

where $N(0)$ is the density of states for the Kondo problem and the reduction factor R is estimated to be Eqs.(13) and (14). Solving the scaling equations for $J_\perp$ and J_z, an estimate of the Kondo temperature T_K is obtained for large $R(>> 1)$ as

$$T_K \sim t \exp\left[-\frac{RU_{\rm eff.}}{\Delta}\right]. \tag{16}$$

This Kondo temperature gives the effective bandwidth B in the large-d model, and the effective mass enhancement is estimated as $m^*/m = t/T_K \sim \exp\left[\frac{RU_{\rm eff.}}{\Delta}\right]$. This strong mass enhancement manifests itself in the physical quantities as follows. The orbital susceptibility $\chi_\eta(i\omega_n \to \omega + i\delta)$ has a peak at $\omega = 0$ with the peak height of the order of η_0^2/T_K and with the width of the order of T_K. The specific heat coefficient γ should be proportional to B^{-1}, while the coefficient A of T^2 in Eq.(1) scales as $A \propto B^{-2}$. The ferromagnetic transition temperature T_c is expected to be proportional to B, and hence we expect a large isotope effect when $R > 1$. In other words, the large isotope effect does not rule out the large Coulomb interaction U. The edge of the photoemission spectrum at the Fermi energy and the Drude weight are reduced by the factor m/m^*. As mentioned above, many experiments except for those of specific heat seem to suggest that the manganese oxides in their ferromagnetic state belong to the strongly correlated region. Then it is natural that the large isotope effect is observed. The band width is rather difficult to pin down accurately, but a rough estimate from A in eq.(1) is $B \sim 0.1$eV , which is comparable to Ω. This suggests that the suppression is not extremely large. Another experimental fact is that the temperature independent Jahn-Teller phonon is observed at the frequency near the original one [12], which means that U is larger or at least of the order of $E_{\rm LR}$. Then we conclude that the relative magnitude of the energy scales is $\Omega < E_{\rm LR} < U$ for the ferromagnetic phase in the manganese oxides. The small specific heat coefficient necessitates the physical mechanisms which have not been included in our model. One possibility is the inter-site process like the

orbital singlet formation, and another possibility is that the proximate quantum criticality is affecting the Fermi liquid behavior.

In summary, we have studied a model of manganese oxides in the ferromagnetic state taking into account both the Coulomb repulsion U and the Jahn-Teller interaction $E_{\rm LR}$. These two interactions collaborate to induce the local orbital moments. In the strong coupling case, i.e., $U_{\rm eff.} = U + 4E_{\rm LR} >> t$ (t : transfer integral), the overlap of the phonon wavefunctions ($\sim e^{-E_{\rm LR}/\Omega}$) enters the tunneling amplitude between the two minima for the orbital moment. The phonon spectral function consists of two parts, i.e., the sharp peak at the renormalized frequency $\tilde{\Omega} = \Omega\sqrt{U_{\rm eff.}/U}$ and the broad peak with the width of the order of the band width. These results can reconcile the large isotope effect on T_c and the apparent temperature independent phonon spectrum assuming $U > E_{\rm LR} > \Omega$.

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